

“नामुमकिन कुछ भी नहीं है हम वह सब कर सकते हैं जो हम सोच सकते हैं और वह सब सोच सकते हैं जो हमने कभी नहीं सोचा।”

CSIR NET – Life Science

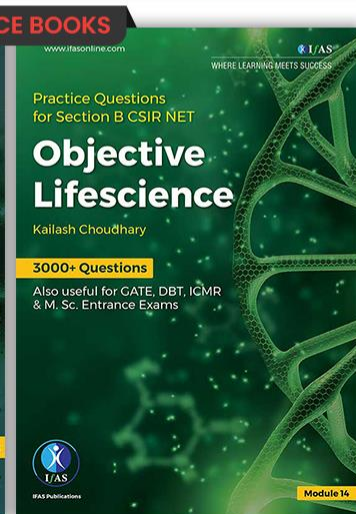
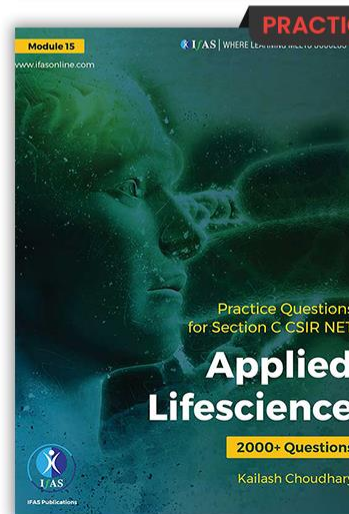
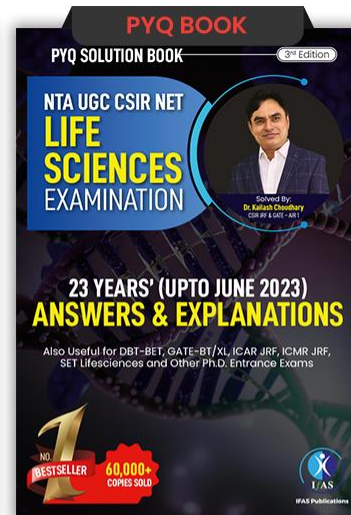
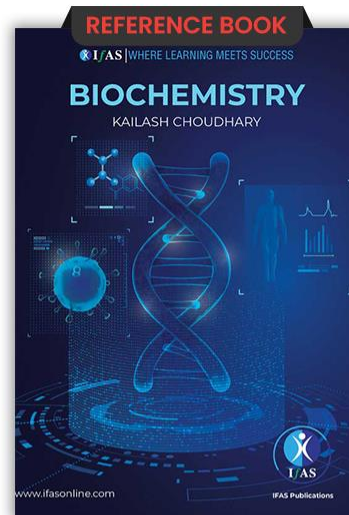
Unit 1: Biochemistry

04

pH and Buffer



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Points to be covered in this Lecture

 What are acid and Bases?



 Ionic Product of Water



 What is pH?



 pH of Acid and Base



 K_a and pK_a



 Buffers





Basics of log calculations

Number	Logarithm
1	0
2	0.3
3	0.48
4	0.6
5	0.7
6	0.78
7	0.86
8	0.9
9	0.95
10	1.0

Number	Logarithm
10^0	0
10^1	1
10^2	2
10^3	3
10^{-1}	-1
10^{-2}	-2
10^{-3}	-3
$10^{2.2}$	2.2
$10^{-2.5}$	-2.5
10^{-6}	-6

$\frac{1}{10} \rightarrow 10^{-1}$
 $\frac{1}{100} \rightarrow 10^{-2}$

$$\begin{aligned} \log 1 &= 0 \\ \log 10 &= 1 \\ \log 100 &= 2 \\ \log 1000 &= 3 \\ \log \frac{1}{10} &= -1 \\ \log \frac{1}{100} &= -2 \end{aligned}$$



Calculate

Log of 50

$$\log 5 \times 10$$

$$\log 5 + \log 10$$

$$= 0.7 + 1$$

$$= 1.7$$

Log 1/20

$$\log 1 - \log 20$$

$$0 - \log 20$$

$$-(\log 20)$$

$$-(\log 2 \times 10)$$

$$-(\log 2 + \log 10)$$

$$-(0.3 + 1)$$

$$-(1.3)$$

$$-1.3$$

(Log 0.2)

$$\log \frac{2}{10}$$

$$\log 2 - \log 10$$

$$= 0.3 - 1$$

$$= -0.7$$

$$\checkmark \log \frac{1}{5}$$

$$= -0.7$$



Calculate

$$\text{Log } 5.05 \times 10^{-5}$$

$$\text{Log } 5 \times 10^{-5}$$

$$\log 5 + \log 10^{-5}$$

$$= 0.7 - 5$$

$$= -4.3$$

$$\text{Log } \underline{4.05} \times 10^{-6}$$

$$\log 4 \times 10^{-6}$$

$$\log 4 + \log 10^{-6}$$

$$= 0.6 - 6$$

$$= -5.4$$



Antilog

What is antilog of 2? $\rightarrow 100$

What is antilog of -1? $\rightarrow \frac{1}{10}$ or 10^{-1}

What is antilog of 0.6? $\rightarrow 4$

What is antilog of -0.7? $\rightarrow \frac{1}{5}$ or 0.2 or 2×10^{-1}

What is antilog of 1.3?

$$\begin{array}{rcl} \text{Antilog } 1 & + & \text{Antilog } 0.3 \\ 10 & \times & 2 = 20 \end{array}$$

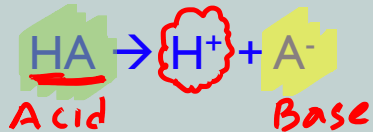
$$\begin{array}{rcl} \text{Antilog } 1.6 & & \\ 10 \times 4 = 40 & & \end{array}$$

$$\begin{array}{rcl} \text{Antilog } -2.7 & & \\ = \frac{1}{100 \times 5} & & \\ = \frac{1}{500} & & \end{array}$$

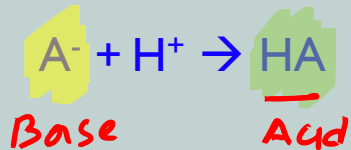


What is acid and Base?

Any hydrogen-containing substance that is capable of donating a proton (hydrogen ion) to another substance *or water*



A base is a molecule or ion able to accept a hydrogen ion from an acid.



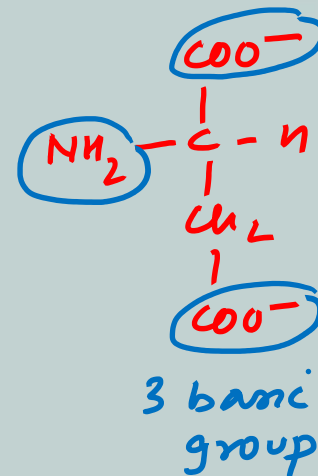
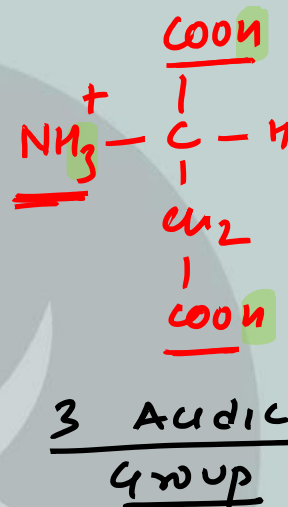
- Acid donate H^+
- Acid accept electron
- Acid pH is less than 7
- Acid is sour in taste

- Accepts H^+
- donate electron
- pH is higher than 7



Example of Acid and its Conjugate Base

Acid	Conjugate Base
<u>HCl</u>	<u>Cl⁻</u>
<u>Acetic Acid (CH₃COOH)</u>	<u>Acetate (CH₃COO⁻)</u>
<u>CO₂ (H₂CO₃)</u>	<u>Bicarbonate (HCO₃⁻)</u>
<u>Citric Acid</u>	<u>Citrate</u>
<u>Formic Acid</u>	<u>Formate</u>
<u>Lactic Acid</u>	<u>Lactate</u>
<u>Ammonium Ion (NH₄⁺)</u>	<u>Ammonia (NH₃)</u>





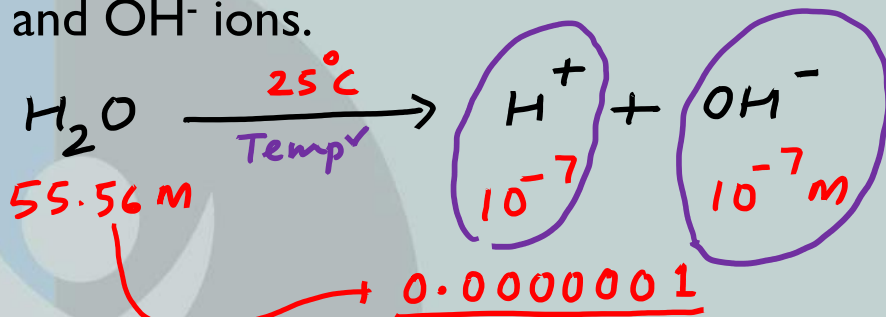
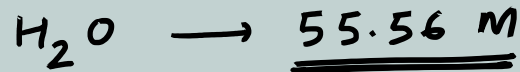
Ionic product of water (K_w)

The product of concentration of H^+ ion and OH^- ions.

$$K_w = [H^+][OH^-]$$

$$= (1 \times 10^{-7})(1 \times 10^{-7})$$

$$K_w = 1 \times 10^{-14} \quad 25^\circ C$$



Temp^v ↑ : more dissociation

Temp^v ↓ : lesser dissociation



If concentration of H^+ is given concentration of OH^- can be calculated and vice-versa

$$K_w = 10^{-14} \text{ m}^2$$

$$(H^+) = \frac{10^{-14}}{(OH^-)}$$

$$(OH^-) = \frac{10^{-14}}{[H^+]}$$

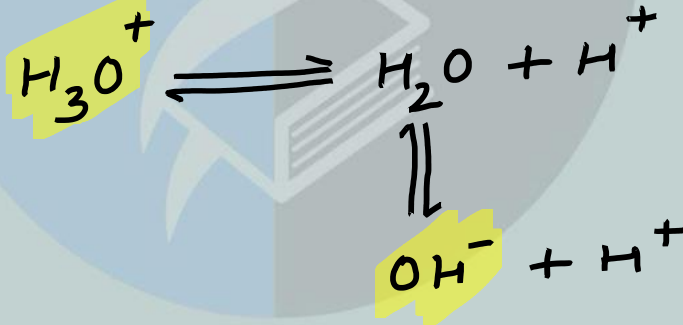
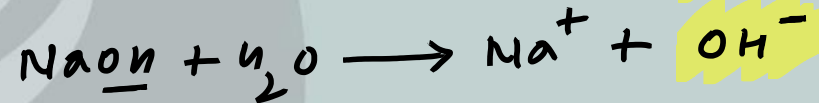
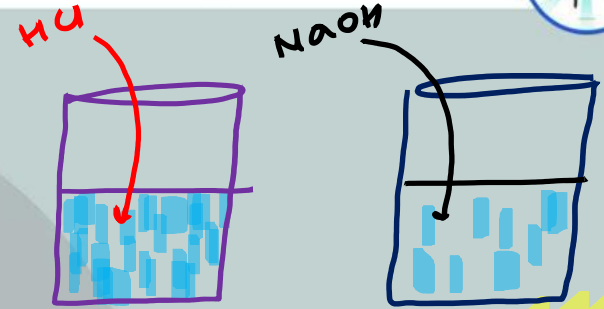
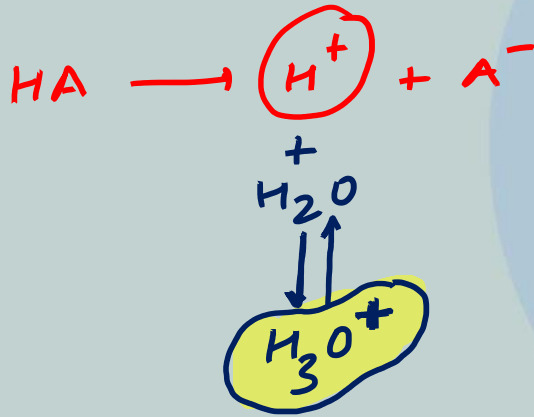
$$K_w = (H^+) \times (OH^-)$$

$$10^{-14} = (H^+) \times (OH^-)$$



Acid or Base in aqueous environment

- Only one acid in water of H_3O^+ ion
- Only one base in water OH^- ions

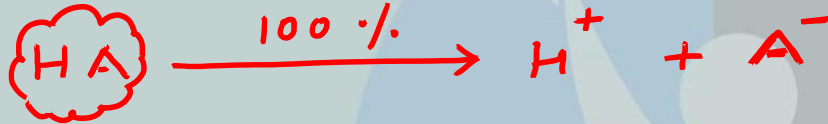




Strong acid and Weak Acids

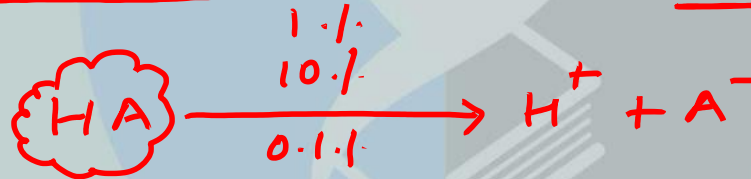
A strong acid fully dissociates (100 %) into its ions in water.

Eg. HCl, HI



A weak acid partially dissociated into its ions in an aqueous solution or water.

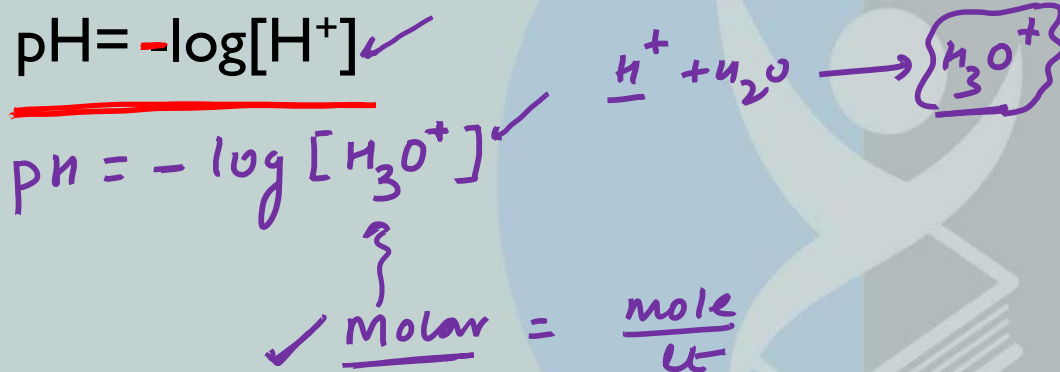
Eg. Acetic Acid
Formic Acid
Citric Acid





What is pH?

- Power of hydrogen *in aqueous solution*
- Inverse relationship with H^+ concentration
- $pH = -\log[H^+]$ ✓



$$\begin{aligned}
 pH &\propto \frac{1}{[H^+]} \\
 pH &= \log \frac{1}{[H^+]} \\
 pH &= \log 1 - \log(n^+) \\
 &= 0 - \log(n^+) \\
 &= -\log(n^+)
 \end{aligned}$$



Apply your mind:

Question: A strong acid solution with pH 4 was diluted to 100 times, what will be the pH of diluted solution?

(1) 2

(2) 4

☒ (3) 6

(4) 8

100 times dilution (10^2)



$H^+ = \downarrow$ $pH = \uparrow$

pH will increase by 2 units



Apply your mind:

The pH of cytosol is 7.2 and the pH of lysosome is 4.2. The cytosol has a $[H^+]$ that is

- (1) 10 times lower than that of lysosome
- (2) 0.1 times lower than that of lysosome
- (3) 100 times lower than that of lysosome
- (4) 1000 times lower than that of lysosome.

10 fold gradient
100 " "
1000 " "
10,000 " "

pH change
1 unit
2 unit
3 unit
4 unit

pH

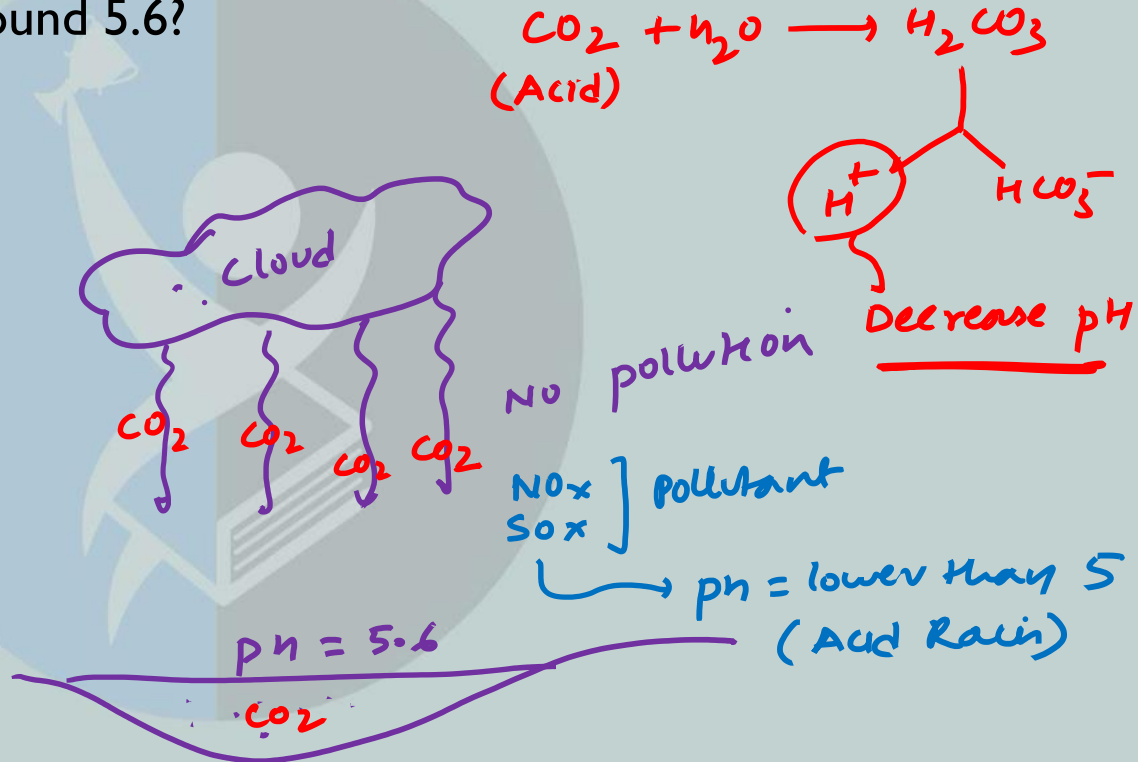
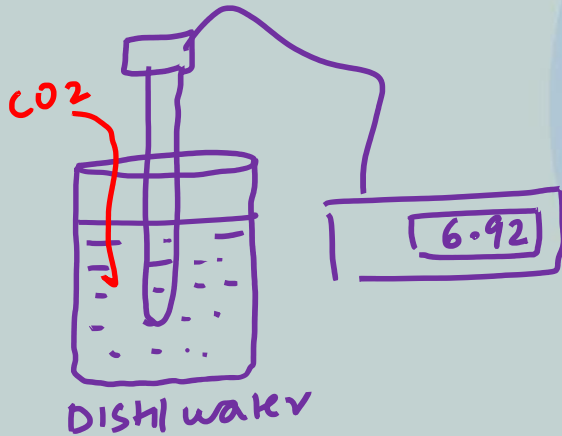
Cytosol
7.2
 $H^+ = \downarrow$

Lysosome
4.2
 $H^+ = \uparrow$

Difference 3 unit
 $Conc^v = 1000$ fold variation

Why pH of distilled water kept in beaker under pH meter is not exactly 7?

Why the pH of rain water is around 5.6?





pH of mono-protonic strong acid

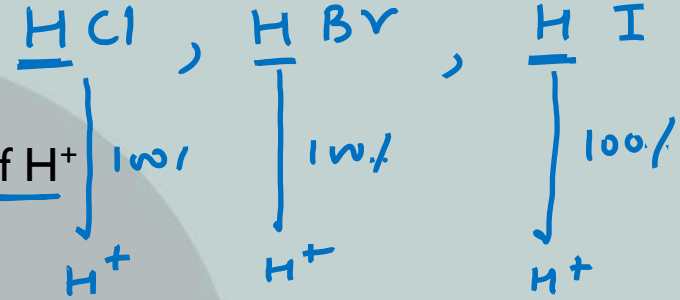
Acid concentration directly provide concentration of H^+

$$pH = -\log[H^+]$$

- 0.1 M HCl ?

$$H^+ = 0.1 \text{ or } 10^{-1}$$

$$\begin{aligned} pH &= -\log(H^+) \\ &= -\log 10^{-1} \\ &= -(-1) \\ &= 1 \end{aligned}$$





Apply your mind:

Question: Calculate pH of 1mM HCL

$$\begin{aligned}(\text{H}^+) &= 1 \text{ mM} \\ &= 1 \times 10^{-3} \text{ M} \\ &= 10^{-3} \text{ M}\end{aligned}$$

$$\begin{aligned}\text{pH} &= -\log [\text{H}^+] \\ &= -\log 10^{-3} \\ &= -(-3) \\ &= +3\end{aligned}$$



pH of multi-protonic strong acid

Concentration of H^+ = Acidity x Acid concentration

$$pH = -\log[H^+]$$

$$= -\log 2 \times 10^{-3}$$

$$= -(\log 2 + \log 10^{-3})$$

$$= -(0.3 - 3)$$

$$= -(-2.7)$$

$$= +2.7$$

Acidity =



2

3

• pH of 1 mM H_2SO_4

$$H^+ = 2 \times 1 \text{ mM}$$

$$= 2 \text{ mM}$$

$$= 2 \times 10^{-3} \text{ M}$$

**Apply your mind:**

Calculate pH of 0.05 M H_2SO_4 ?

(1) 0.7

☒ (2) 1

(3) 1.3

(4) 2

$$\text{Normality} = \text{H}^+ \text{ conc}^r$$

= of Acid

$$\begin{aligned} [\text{H}^+] &= 2 \times \text{Acid conc}^r \\ &= 2 \times 0.05 \text{ M} \\ &= 0.1 \text{ M} = 10^{-1} \text{ M} \end{aligned}$$

$$\begin{aligned} \text{pH} &= -\log 10^{-1} \\ &= -(-1) \\ &= +1 \end{aligned}$$



pH of strong base:

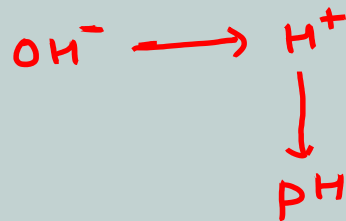
$$\text{pOH} = -\log[\text{OH}^-]$$

$$\text{pOH} = \log \frac{1}{(\text{OH}^-)}$$

$$[\text{OH}^-] \longrightarrow \text{pOH}$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - \text{pOH}$$



$$[\text{H}^+] = \frac{10^{-14}}{(\text{OH}^-)}$$



Apply your mind:

Question: Calculate the **pH** of 0.1 M Base KOH

- (1) 1
- (2) 6.98
- (3) 7.02
- ✓ (4) 13

Acid pH is
always lesser than 7

Base pH is
always higher than 7
at 25°C

$$\text{OH}^- = 0.1 = 10^{-1}$$

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] \\ &= -\log 10^{-1} \end{aligned}$$

$$\text{pOH} = 1$$

$$\begin{aligned} \text{pH} &= 14 - \text{pOH} \\ &= 14 - 1 \\ &= 13 \end{aligned}$$

$$\text{H}^+ = \frac{10^{-14}}{(\text{OH}^-)}$$

$$\text{H}^+ = \frac{10^{-14}}{10^{-1}}$$

$$\text{H}^+ = 10^{-13}$$

$$\text{pH} = -\log (\text{H}^+)$$

$$\begin{aligned} \text{pH} &= -\log 10^{-13} \\ &= -(-13) \end{aligned}$$

$$= 13$$



Apply your mind:

The (OH⁻) of 0.1 N HCl solution will be

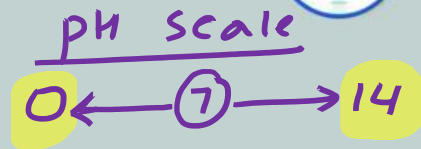
$$\begin{aligned} & \downarrow \\ H^+ &= 10^{-1} \\ [OH^-] &= \frac{10^{-14}}{[H^+]} \\ &= \frac{10^{-14}}{10^{-1}} \\ &= 10^{-13} \end{aligned}$$

$$\begin{aligned} pH &= 1 \\ pOH &= 14 - 1 \\ pOH &= 13 \\ [OH^-] &= 10^{-13} \end{aligned}$$

$$(H^+) \times (OH^-) = 10^{-14}$$



Theoretically pH can be *Acid is highly concentrated* less than zero (negative)



Calculate pH of 10 M HCL solution?



$$\begin{aligned} pH &= -\log 10 \\ &= -1 \end{aligned}$$

Calculate pH of 100 M HBr solution?



$$\begin{aligned} pH &= -\log (100) \\ &= -2 \end{aligned}$$



pH of aqueous solutions ranges from **0-14** at 25° C

But pH of **pure water** can also vary with **temperature**



At lower temperature pH + pOH can be higher than 14

At higher temperature pH + pOH can be lower than 14

$$\downarrow \text{pH} \propto \frac{1}{\text{Temp}^\circ} \uparrow \quad \downarrow \text{pOH} \propto \frac{1}{\text{Temp}^\circ} \uparrow$$

$$\left. \begin{array}{l} \text{H}^+ = \uparrow \quad \text{pH} = \downarrow \\ \text{OH}^- = \uparrow \quad \text{pOH} = \downarrow \end{array} \right\}$$

Sum of pH + pOH
will be less than
14



10^{-8} M
 pH of Very dilute solution of strong acid
HCl

Total H^+ Concentration will be

- H^+ from dilute acid and H^+ of water (10^{-7} M)
- It would be slightly **lesser than 7**

$$\text{pH} = -\log (\text{Total } \text{H}^+)$$

$$\begin{aligned} & \frac{10^{-8} \text{ M}}{(\text{H}^+)_{\text{HCl}}} = 0.00000001 \text{ M} (10^{-8}) \\ & (\text{H}^+)_{\text{H}_2\text{O}} = 0.0000001 \text{ M} (10^{-7}) \end{aligned}$$



Apply your mind:

Calculate pH of 10^{-8} M HCl (Given $\log 1.1 = 0.04$)

(1) 6.96

(2) 7.04 ✗

(3) 7.0 ✗

(4) 8.0 ✗

Aud pH must be lower than 7.

$$\begin{aligned} H^+_{HCl} &= 10^{-8} \text{ M} \\ H^+_{H_2O} &= 10^{-7} \text{ M} \end{aligned}$$

$$\begin{aligned} pH &= -\log (H^+) \\ &= -\log 10^{-8} \\ &= 8 \end{aligned}$$

← Not possible for acid

$$\begin{aligned} pH &= -\log 1.1 \times 10^{-7} \\ &= -\log 1.1 + \log 10^{-7} \\ &= -(0.04 - 7) \\ &= -(-6.96) \\ &= 6.96 \end{aligned}$$

$$\begin{aligned} \text{Total}(H^+) &= 10^{-8} + 10^{-7} \\ &= (10^{-1} \times 10^{-7}) + (1 \times 10^{-7}) \\ &= 0.1 \times 10^{-7} + 1 \times 10^{-7} \\ &= (0.1 + 1) \times 10^{-7} \\ &= 1.1 \times 10^{-7} \end{aligned}$$

**Apply your mind:**

Calculate the pH of 10^{-8} M NaOH solution?

- (1) 4 ✗
- (2) 6.96 ✗
- ✓ (3) 7.04
- (4) 10 ✗

Base

Low concⁿ

$$\text{pOH} = -\log 10^{-8} \\ = 8$$

$$\text{pH} = 14 - 8$$

$= 6 \rightarrow$ which is not possible for base

must be higher than 7



pH of mixture of two acidic solution when added in equal volume

- pH depends on H⁺ ion from solution 1 + solution 2
- ✓ • It will be between pH of solution 1 and solution 2
- ✓ • pH will be not average
- It will be closer to strong acidic solution (near lower pH)

Handwritten calculation and diagram:

pH 3 + pH 5
100 ml 100 ml

Diagram showing a number line from 3 to 5. A point 3 is circled, and a point 4 is circled. A double-headed arrow connects 3 and 5. A single-headed arrow points from 3 to 4, and another from 4 to 5, indicating the midpoint.

Answer : 3.3

$$\frac{3+5}{2} = \frac{8}{2} = 4$$



Apply your mind:

What will be of mixture if you add 100 mL of pH=2 HCl solution and 100 mL of pH=4 HCl solution?

- ~~(1) 2~~
- ☒ (2) 2.3
- ~~(3) 3.0~~
- ~~(4) 3.7~~

- In betⁿ 2 to 4
- It will not be average i.e 3
- It would near to 2

provides more H^+



pH of mixture of two basic solution when added in equal volume

- pH depends on H^+ ion from solution 1 + solution 2 $pH = 8$ $pH = 10$
- It will be between pH of solution 1 and solution 2 betⁿ 8 to 10
- pH will be not average \neq 9
- It will be closer to strong basic solution (higher pH)
 \nearrow near 10
 \downarrow provide more OH^-



What will be of mixture if you add 100 mL of pH=8 NaOH solution and 100 mL of pH=12 NaOH solution?

- (1) 8.0
- (2) 8.3
- ~~(3) 10.0~~
- ☒ (4) 11.7

pH = 8

pH = 12

• in betⁿ 8 to 12

• will not be average $\frac{12+8}{2} = \frac{20}{2} = 10$

• Near strong base (pH=12)



pH of mixture of acid + base solution when added in Equal Volume

- pH depends on H^+ ion from solution 1 + OH^- ion solution 2
- It will be in between pH of solution 1 and solution 2
- pH will be average ✓
- It will be closer to 7 ✓

$$\frac{4 + 10}{2} = \frac{14}{2} = 7$$



Apply your mind:

If 500 ml of pH 3 and 500 ml of pH 11 solution are mixed, then what would be resultant pH of mixture?

- ☒ (1) 7.0
- (2) 3.3
- (3) 10.7
- (4) 3.0

500 mL pH = 3 Acid
500 mL pH = 11 Base

$$pH = \frac{3 + 11}{2} = \frac{14}{2} = 7$$



Ka of weak acid

Dissociation constant for acid



$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$H^+ = \sqrt{K_a \cdot [HA]}$$

$$pH = -\log(H^+)$$

- ✓ High K_a means strong acid
- ✓ Low K_a means weak acid



$$pK_a = -\log K_a$$

$$pH \propto \frac{1}{[H^+]}$$

$$pK_a \propto \frac{1}{K_a}$$

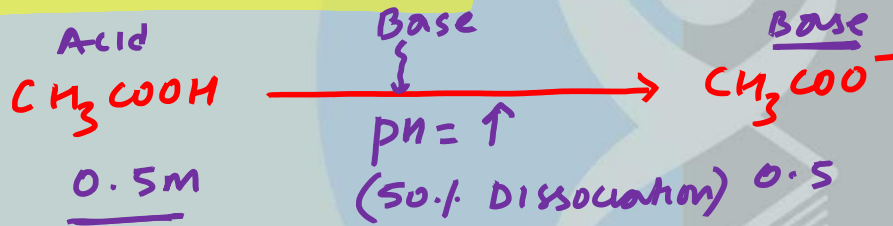
$$pH = \log \frac{1}{[H^+]}$$

$$pK_a = \log \frac{1}{K_a}$$

$$pH = -\log [H^+]$$

$$pK_a = -\log K_a$$

pKa is a **pH** at which the concentration of **weak acid** and its **conjugate base** will be in **equimolar concentrations**.



- Strong acid has low pKa , Higher K_a
- Weak acid has higher pKa , low K_a

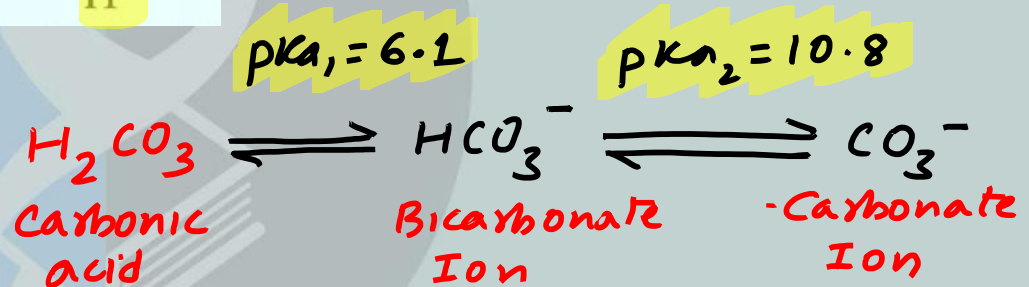
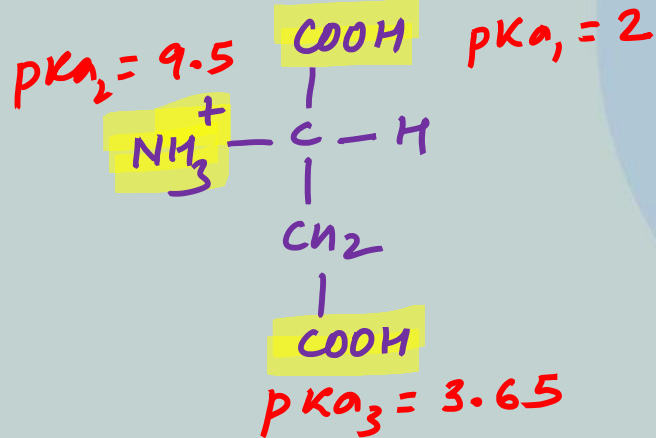
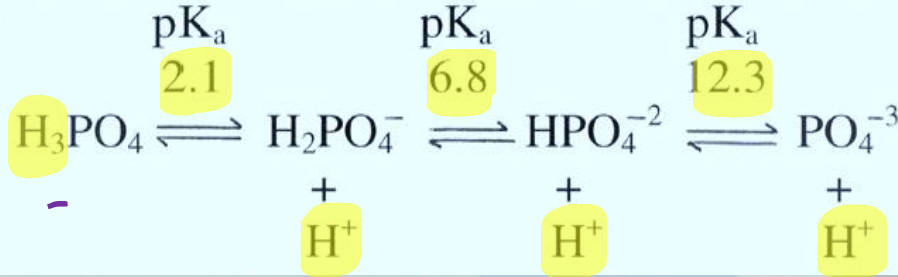


- Formic acid
- Lactic acid
- Pyruvic acid



Poly-protonic acid has Multiple pKa

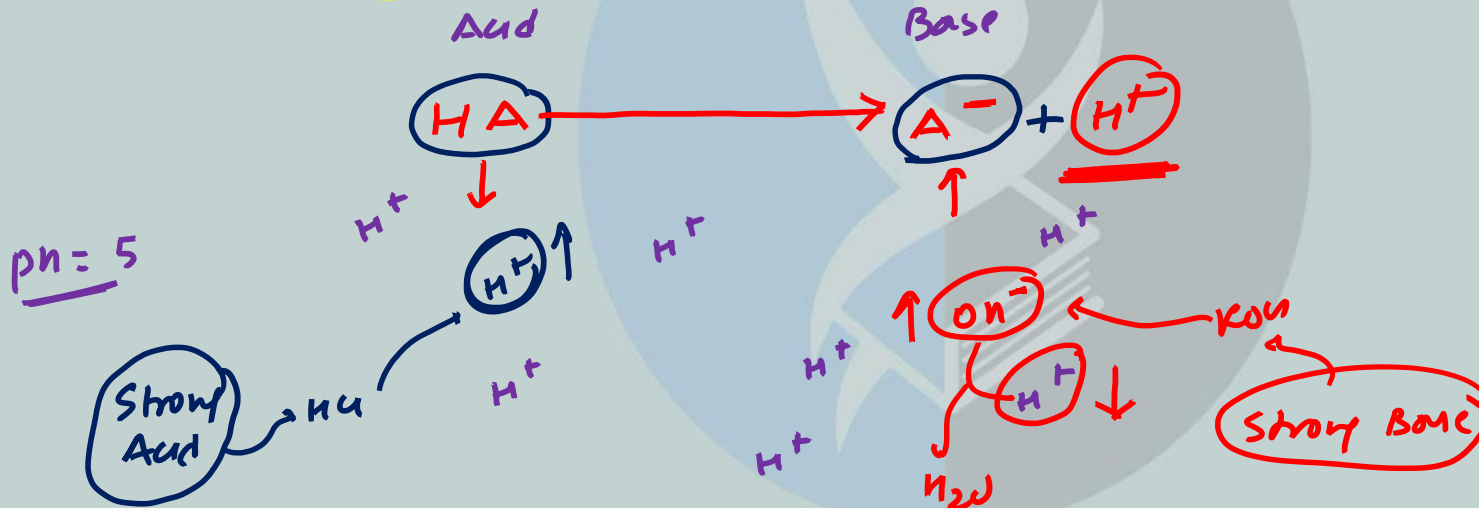
$$\begin{aligned} pK_{a1} &= 2.1 \\ pK_{a2} &= 6.8 \\ pK_{a3} &= 12.3 \end{aligned}$$





What are buffers?

- It is mixture of weak acid and its conjugate base
- Retard the change in the pH of a solution on addition of strong acids or strong bases.



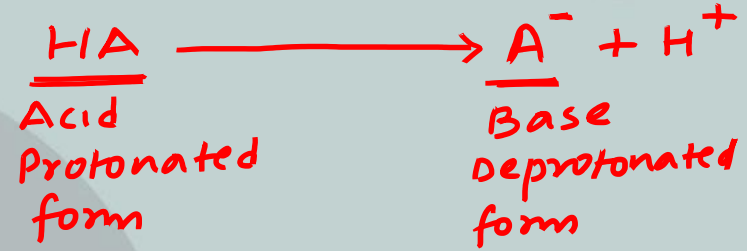


Henderson - Hasselbalch equation :

$$\text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]}$$

\leftarrow Base form
 \leftarrow Acid form

of weak acid



- Best Buffering is when pH of buffer is equal to pKa of weak acid
- General Buffering range is $\text{pH} = \text{pK}_a \pm 1$
- When there is more than one pKa choose pKa closest to desired pH

$$[\text{Acid}] = [\text{Base}]$$

$$\log 1 = 0$$

$$\text{pH} = \text{pK}_a$$

Acetic acid ($\text{pK}_a = 4.76$) \rightarrow Best buffer $\text{pH} = 4.76$

$$\hookrightarrow \text{Buffer Range} = 4.76 \pm 1 = 3.76 \text{ to } 5.76$$



How to make buffer of required pH if pKa of acid is given?

What must ratio of base to acid?

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

← Base
← Acid

- [base] > [acid] means pH > pKa
- [base] = [acid] means pH = pKa
- [base] < [acid] means pH < pKa

<u>Base</u> <u>Acid</u>	<u>pH</u>
10 : 1	pKa + 1
100 : 1	pKa + 2
1000 : 1	pKa + 3
<hr/>	
1 : 10	pKa - 1
1 : 100	pKa - 2
1 : 1000	pKa - 3



Apply your mind:

Prepare a 0.2 M acetate buffer with pH 4.76 (pKa=4.76)

- ✓ (1) 0.1 M Acetate + 0.1 M Acetic acid
- (2) 0.1 M Acetate + 0.01 M Acetic acid
- (3) 0.01 M Acetate + 0.1 M Acetic acid
- (4) 0.1 M Acetate + 0.2 M Acetic acid

Base

Acid

$$pH = pKa + \log \frac{\text{Acetate}}{\text{Acetic acid}}$$

$$pH - pKa = \log \frac{\text{Acetate}}{\text{Acetic acid}}$$

$$\text{Antilog} (pH - pKa) = \frac{\text{Acetate}}{\text{Acetic acid}}$$

$$\text{Antilog} (4.76 - 4.76) = \frac{\text{Base}}{\text{Acid}}$$

$$pH = pKa$$

$$\text{Base} = \text{Acid}$$

$$\text{Antilog } 0 = \frac{\text{Base}}{\text{Acid}}$$

$$1 = \frac{\text{Base}}{\text{Acid}}$$



Apply your mind:

Prepare Acetate buffer with pH 5.76 (pKa=4.76)

(1) 0.1 M Acetate + 0.1 M Acetic acid ✗

✓ (2) 0.1 M Acetate + 0.01 M Acetic acid

(3) 0.01 M Acetate + 0.1 M Acetic acid ✗

(4) 0.1 M Acetate + 0.2 M Acetic acid ✗

$$pH = pK_a + \log \frac{B}{A}$$

$$\textcircled{5.76} = 4.76 + \log \frac{B}{A}$$

$$= 4.76 + \log 10$$

$$= 4.76 + 1$$

$$\frac{Base}{Acid} = \frac{0.1}{0.01} = \frac{10}{1}$$

$$\text{Antilog}(pH - pK_a) = \frac{Base}{Acid}$$

$$\text{Antilog}(5.76 - 4.76) = B/A$$

$$\text{Antilog } 1 = B/A$$

$$\frac{10}{1} = B/A$$



Apply your mind:

100 mL of 0.1 M sodium acetate has pH of 8.9. To this solution 1 mL of 1 M acetic acid (pKa = 4.76) of pH 2.80 is added. The pH of resultant mixture will be?

- (1) 8.9
- (2) 3.76
- (3) 4.76
- ✓ (4) 5.76

Base → 100 mL 0.1 M 0.1 mole / 1000 mL

$$1000 \text{ mL} = 0.1$$

$$1 \text{ mL} = \frac{0.1}{1000}$$

Base → $\frac{100 \text{ mL}}{1000} = \frac{0.1}{1000} \times 100 = 0.01 = 10^{-2} \text{ mole}$

1 mL → 1 M 1 mole / 1000 mL

$$1000 \text{ mL} \rightarrow 1 \text{ mole}$$

$$1 \text{ mL} \rightarrow \frac{1}{1000} \text{ mole} = 10^{-3} \text{ mole}$$

$$\begin{aligned} \text{pH} &= \text{pKa} + \log \frac{\text{Acetate}}{\text{Acetic acid}} \\ &= 4.76 + \log \frac{10^{-2}}{10^{-3}} \\ &= 4.76 + \log 10^1 \\ &= 4.76 + 1 = 5.76 \end{aligned}$$



If pH of buffer is given we can estimate base/acid ratio

$$\underline{pH} = \underline{pK_a} + \log \frac{[A^-]}{[HA]}$$

Antilog $(pH - pK_a) = \frac{\text{Base}}{\text{Acid}}$

Calculate [base]/[acid] ratio using this equation.

$$\frac{[\text{Base}]}{[\text{Acid}]} = \frac{[A^-]}{[HA]} = \underline{\text{Antilog}} (\underline{pH} - \underline{pK_a})$$



Apply your mind

The apparent pH of a fluid is 7.45, where bicarbonate buffer is involved for maintaining its pH. Values of pKa of carbonic acid are 6.15 and 10.45. The molar ratio of [conjugate base]:[acid] is (Hint: antilog 1.3 = 20.0, and antilog $10^3 = 1000$)

(1) 1: 20

(2) 20: 1

(3) 1: 1000

(4) 1000: 1

$pK_{a1} = 6.15$ ✓

$pK_{a2} = 10.45$ ✗

$pH = 7.45$

$pK_a = 6.15$

$$\text{Antilog}(pH - pK_a) = \frac{\text{Base}}{\text{Acid}} = \frac{HCO_3^-}{CO_2} = \frac{20}{1}$$

$$\text{Antilog}(7.45 - 6.15) = B/A$$

$$\text{Antilog } 1.3 = B/A$$

$$20/1 = B/A$$



Degree of protonation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Deprotonated form}] \leftarrow \text{A}^-}{[\text{Protonated form}] \leftarrow \text{HA}} \quad \frac{1}{10}$$

$$\text{Total} = \text{P} + \text{DP}$$

$$11 = 10 + 1$$

$$\text{P} = \frac{10}{11} \times 100 = 90\%$$

$$\text{DP} = \frac{1}{11} \times 100 = 10\%$$

pH and pKa	Base/Acid Ratio	Deprotonated Form	Protonated Form
pH=pKa	1:1	50%	50%
pH= pKa -1	1:10	10%	90%
pH=pKa-2	1:100	1%	99%
pH=pKa+1	10:1	90%	10%
pH=pKa+2	100:1	99%	1%

lower pH

higher pH



Apply your mind

100 ml of 0.02 M acetic acid ($pK_a = 4.76$) is titrated with 0.02 N KOH. After adding some base to the acid solution, the observed pH is 2.76. At this pH degree of protonation is

(1) 0% ~~X~~

(2) 10% ~~X~~

(3) 90%.

☒ (4) 99%.

Solution :

$$\text{Antilog}(pH - pK_a) = \frac{DP}{P}$$

$$\text{Antilog}(2.76 - 4.76) = \frac{DP}{P}$$

$$\text{Antilog} -2 = \frac{DP}{P}$$

$$\frac{1}{100} = \frac{DP}{P}$$

$$DP : P = \text{Total}$$

$$1 : 100 = 101$$

$$P = \frac{100}{101} \times 100 = 99\%$$

$$pH = 2.76 < pK_a = 4.76$$

Protonated form will be more than 50%.

$$pH = pK_a - 2$$



Buffers are independent of limited dilution

- 10 fold or 100 fold dilution of buffer with water will not change pH
- Because concentration of base form and acid form both get diluted

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad \xrightarrow{\substack{\text{100 fold} \\ \text{Dilution}}} \quad \frac{0.1 \text{ M} \cdot \frac{0.1}{100}}{0.1 \text{ M} \cdot \frac{0.1}{100}} = \frac{0.01}{0.01} = 1$$

$$pH = 5 + \log \frac{0.1}{0.1}$$

$$pH = 5$$

$$pH = pK_a + \log 1$$

$$pH = 5 + 0$$

$$pH = 5$$



Apply your mind

One litre of 0.2 M acetate buffer of pH=4.76 ($pK_a=4.76$) was dilute 10 times, what will be altered pH?

(1) 3.76

✓ (2) 4.76

(3) 5.76

(4) 6.76

$$\begin{array}{lcl} pH = pK_a & \text{Base} = \text{Acid} & = \text{Buffer} \\ & \left(\frac{0.1}{10} \quad \frac{0.1}{10} \right) & 0.2M \\ & \downarrow \quad \downarrow & \\ & 0.01 \quad 0.01 & = 0.02M \end{array}$$

$$\begin{aligned} pH &= pK_a + \log \frac{B}{A} \\ &= 4.76 + \log \frac{0.01}{0.01} \\ &= 4.76 + \log 1 \\ &= 4.76 \end{aligned}$$



Very high dilution affects pH of buffer

- Million fold or 10 Million fold dilution of buffer with water change pH
- Because concentration of base form and acid form in buffer become lesser than 10^{-7} M.
- Thus, H_3O^+ and OH^- of water will decide buffer
- It will closer to 7
 - For acidic buffer on high dilution it will be slightly lesser than 7
 - For basic buffer on high dilution it will be slightly higher than 7



Apply your mind

10 mM acetate buffer (pH 4.00) is diluted one million times with distilled water (pH 7.00). pH of this diluted buffer is:

(1) 4.00 ✗

(2) 7.04 ✗

(3) 8.00 ✗

✓ (4) 6.96

(Help: $\log_{10} 10^x = x$; $\log_{10} 1.10 = 0.04$; $\log_{10} 1.01 = 0.004$)

$$\begin{aligned} \frac{10 \times 10^{-3} \text{ M}}{10^6} &= 10^{-2} \text{ M} \\ \text{pH} &= \frac{10^{-2}}{10^6} = 10^{-8} \end{aligned}$$



Buffer strength (Molarity) depends on moles/l of acid form and base form?

100 mL of 1 M Acetic acid + 100 mL of 1 M Acetate = pH of buffer = 4.76

100 mL of 1 mM Acetic acid + 100 mL of 1 mM Acetate = pH of buffer = 4.76

pH is same but strength is not same

Strength of first buffer is more



Apply your mind

A buffer is prepared by mixing 50 ml of 0.20 M acetic acid and 50 ml of 0.20 M sodium acetate. The pH of the buffer is 4.75 which is equal to the value of pKa of the acid. The molarity of the buffer is

(1) 0.10.

(2) 0.15.

✓ (3) 0.20.

(4) 0.40.

$$0.2 \text{ M} = \frac{0.2 \text{ mole}}{1000 \text{ mL}}$$

$$1000 \text{ mL} \rightarrow 0.2 \text{ mole}$$

$$1 \text{ mL} \rightarrow \frac{0.2}{1000} \text{ mole}$$

$$50 \text{ mL} \rightarrow \frac{0.2}{1000} \times 50 = \frac{10}{1000} = 0.01$$

50 mL 0.2 M acetic acid
50 mL 0.2 M acetate

moles of
acetic acid = 0.01 in 50 mL
acetate = 0.01 in 50 mL

100 mL	Total = 0.02 mole in 100 mL
1000 mL	Total = 0.2 mole in 1000 mL
molarity. = 0.2 M = 0.2 mole/litre	



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